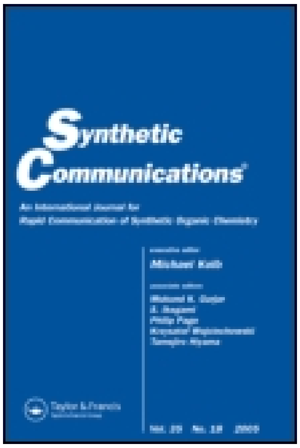

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Unexpectedly High Activity of $Zn(OTf)_2 \cdot 6H_2O$ in Catalytic Friedel–Crafts Acylation Reaction

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Abstract: $Zn(OTf)_2 \cdot 6H_2O$ was used to promote Friedel–Crafts acylation of aromatics. The work describes the high activity and efficiency of $Zn(OTf)_2 \cdot 6H_2O$ in acylation of aromatics, and the catalyst has surpassed most metal triflates in dispensing when dried at high temperature under vacuum before use.

Keywords: Friedel–Crafts acylation, high activity, $Zn(OTf)_2 \cdot 6H_2O$

Despite of their broad utility in organic chemistry, the Friedel–Crafts acylation reaction often needed stoichiometric or even excess of a conventional Lewis acid (LA) such as $AlCl_3$.[1] The formation of a strong coordinate oxygen–metal bond was the key.[2] Thus, the products (ketones) must be obtained after aqueous workup because of the complex of LA with the ketones (Scheme 1).

Although $FeCl_3$[3] allowed the development of a catalytic cycle, drastic conditions were often needed and led to side reactions. Stoichiometric zinc

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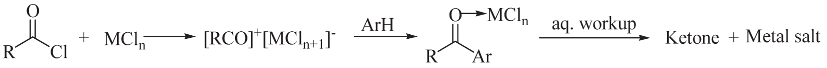


Scheme 1.

power[4] was described as a useful reagent for Friedel–Crafts acylation under microwave irradiation. Because of thier importance in organic chemistry, Friedel–Crafts reactions were well studied using other catalysts.[5] In recent years, Kobayashi et al. found anhydrous rare-earth metal triflates[6] could catalyze the Friedel–Crafts acylation reaction, even using a catalytic amount, with good to excellent yields; later other metal triflates,[7] such as $Hf(OTf)_4$, $Ga(OTf)_3$, $Sb(OTf)_3$, and $Sn(OTf)_2$, also demonstrated high catalytic activity in the Friedel–Crafts acylation reaction. However, it is worth noting that these metal triflates needed activation by drying for a few hours at high temperature under vacuum immediately before use. The same anhydrous condition was needed when aluminium[8] or ferric[9] hydrogensulfate was used as the catalyst. Next, bismuth(III) derivatives[10] were found to be excellent catalysts in the Friedel–Crafts acylation reaction. Among these derivatives, $Bi(OTf)_3 \cdot 4H_2O$ received attention for its surprising catalytic activity in this reaction. Even the inactive fluorobenzene could react with acylation reagents and a catalytic amount of $Bi(OTf)_3 \cdot 4H_2O$ at high temperature with good yield.

However, we found that hexaaqua zinc triflate [$Zn(OTf)_2 \cdot 6H_2O$] was an efficient catalyst for title reaction. Although anhydrous $Zn(OTf)_2$–catalyzed benzoylation and acetylation of anisole in ionic liquid was reported,[11] our experiment had many advantages such as simple operation, moderate reaction condition, and good yields without drying the catalyst at high temperature under vacuum before use.

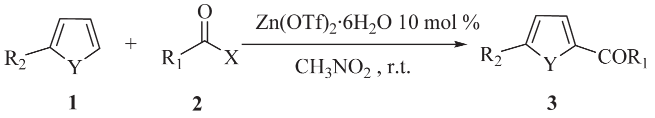
Because zinc triflate is a strong and water-tolerant LA, it can be useful even in practical and industrial applications. In addition, zinc metal was available easily and more cheaply than many other metals. The preparation of $Zn(OTf)_2 \cdot 6H_2O$[12] was easier and simpler than other metal triflates. In continuation of our interest in the Friedel–Crafts reaction,[13] we herein describe a simple and practical method for Friedel–Crafts acylation reaction using $Zn(OTf)_2 \cdot 6H_2O$.

First, we tested the acylation reaction of furan and thiophenes with several acylation reagents in the presence of $Zn(OTf)_2 \cdot 6H_2O$ and the results are summarized in Table 1.

As can be seen in Table 1, the reaction of furan or thiophenes with acylation reagents proceeded smoothly in the presence of $Zn(OTf)_2 \cdot 6H_2O$, but the reactions of thiophenes were a little quicker than those of furan, and thus the yields of acylated thiophenes were higher under the same conditions. In addition, it was obvious that aliphatic acyl chloride reacted with the substrates quicker than aroyl chloride.

It was interesting that the substituent of halogen on the thiophene ring did not affect the yields. For example, 2-chlorothiophene and 2-bromothiophene

Table 1. Friedel–Crafts acylation reaction of furan and thiophenes catalyzed by $Zn(OTf)_2 \cdot 6H_2O$



Entry	Y	X	R_1	R_2	Time (h)	Product	Yield (%)[a]
1	O	$OCOCH_3$	CH_3	H	4	**3a**	75
2	O	Cl	CH_3	H	4	**3a**	85
3	O	Cl	$CH_3CH_2CH_2$	H	4	**3b**	86
4	O	Cl	p-$CH_3C_6H_4$	H	8	**3c**	78
5	S	$OCOCH_3$	CH_3	H	4	**3d**	84
6	S	Cl	CH_3	H	4	**3d**	89
7	S	Cl	CH_3CH_2	H	4	**3e**	89
8	S	Cl	p-$CH_3C_6H_4$	H	8	**3f**	82
9	S	Cl	CH_3	Cl	4	**3g**	87
10	S	Cl	CH_3	Br	4	**3h**	88
11	S	Cl	CH_3	Br	4	**3h**	88[b]

[a] Bazed on aromatics 1.5 mol of acylation reagent was used.
[b] $Yb(OTf)_3$ (5 mol%) was used as the catalyst.

were excellent substrates, which reacted with acetyl chloride quickly and afforded good yields in **4h**. In a contrast, 89% of 5-bromoacetylthiophene was obtained when 5 mol% of anhydrous $Yb(OTf)_3$ was used as the catalyst under the same reaction condition (entry 11).

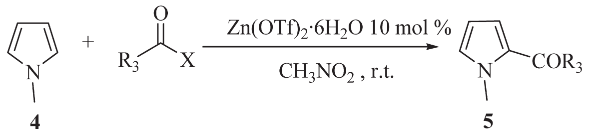
Another five-component heteroaromatic, N-methyl pyrrole, was desirable. We next tested the Friedel–Crafts acylation reaction under different conditions (Table 2). Nitromethane was the best solvent of this reaction. The acylation of N-methyl pyrrole was much easier than other hetero aromatics (including furan and thiophene), and high yield of desirable acetylated and benzoylated products were obtained in **4h**. A long-chain alkyl acyl chloride, named octadecanoyl chloride (n-$C_{17}H_{35}COCl$), was used in the reaction and 78% yield of acylated product was obtained in nitromethane after 12 h at 50°C.

Unfortunately, nicotinoyl chloride (pyridin-3-yl-COCl) afforded less than 10% yield of product. In this case, an insoluble white solid was obtained, which was determined as a hydrochloric compound of pyridines (Scheme 2).

The effects of the solvents were obvious; the best was nitromethane and the worst was carbon tetrachloride (Table 2, entry 11).

In the acylation of anisoles (Table 3), the reaction was slower than those of electron-rich hetero aromatics. Acylated product **7** was dominant, and other isomers were detected in very small parts.

Table 2. Catalytic acylation of N-methyl pyrrole in the presence of $Zn(OTf)_2 \cdot 6H_2O$



Entry	Acylation reagent	Time (h)	Product	Yield (%)[a]
1	Acetic anhydride	4	**5a**	87
2	Acetyl chloride	4	**5a**	92
3	Benzoyl chloride	8	**5b**	86
4	2-Phenyl acetyl chloride	4	**5c**	89
5	Octadecanoyl chloride ($n\text{-}C_{17}H_{35}COCl$)	12	**5d**	78[b]
6	Nicotinoyl chloride (pyridin-3-yl-COCl)	24	**5e**	<10
7	Acetic anhydride	4	**5a**	83[c]
8	Acetic anhydride	4	**5a**	78[d]
9	Acetic anhydride	4	**5a**	65[e]
10	Acetic anhydride	4	**5a**	61[f]
11	Acetic anhydride	4	**5a**	46[g]

[a] Bazed on aromatics. 1.5 mol of acylation reagent was used.
[b] At 50°C for 12 h.
[c] In acetonitrile.
[d] In chloroform.
[e] In dichloromethane.
[f] In nitrobenzene.
[g] In carbon tetrachloride.

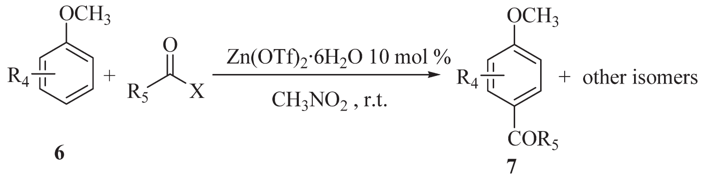
In conclusion, we have found that $Zn(OTf)_2 \cdot 6H_2O$ was a excellent catalyst of the Friedel–Crafts acylation reaction. The work described a facile, simple operation, suitable in large-scale approaches for preparation of aromatic ketones with good yields. The strongest point was the ability to use it without drying at high temperature under vacuum before use.

EXPERIMENTAL

Mass spectra (ESI) were tested on a Thermo Finnagan LCQ Advantage instrument. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian

Scheme 2.

Table 3. Catalytic benzoylation and acetylation of anisoles



Entry	R_4	R_5	X	Time/h	Product	Yield[a]/%
1	*o*-CH_3	CH_3	$OCOCH_3$	8	**7a**	71
2	*o*-CH_3	CH_3	Cl	8	**7a**	78
3	*o*-CH_3	ph	Cl	8	**7b**	72
4	*m*-CH_3	CH_3	Cl	8	**7c**	76
5	*m*-CH_3	ph	Cl	8	**7d**	70

[a] Based on anisole. 1.5 mol of acylation reagent was used.

400-MHz instrument using $CDCl_3$ as the solvent with TMS as an internal standard. IR spectra were recorded on a Avatar-370 infrared spectrophotometer. Melting points were determined on a digital melting-point apparatus WRS-1B and are uncorrected. $Zn(OTf)_2 \cdot 6H_2O$ was prepared according to the literature.[12]

General Procedure for Friedel–Crafts Acyaltion of Aromatics

To a solution of aromatic reagent (4 mmol) and acyaltion reagent (6 mmol) in nitronmethane (5 ml), $Zn(OTf)_2 \cdot 6H_2O$ (0.4 mmol) was added successfully. The mixture was stirred at room temperature for the given time, and it slowly turned green or purple. After completion, it was treated with saturated aqueous $NaHCO_3$ (10 ml) and extracted with chloroform (20 ml × 2). The combined organic solution was dried over anhydrous $MgSO_4$ and filtered. After it was concentrated in vacuum and purified by preparative thin-layer chromatography (TLC), the corresponding product was obtained. The regioselectivity also could be determined by the NMR analysis.

Data

2-Acetylfuran (**3a**)

Oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, $J = 1.7, 0.7$ Hz, 1H), 7.19 (dd, $J = 3.5, 0.7$ Hz, 1H), 6.54 (dd, $J = 3.5, 1.7$ Hz, 1H), 2.49 (s, 3H); IR (cm^{-1}) (neat) 1678.

2-Butyrylfuran (**3b**)

Oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, $J = 1.8, 0.7$ Hz, 1H), 7.19 (dd, $J = 3.7, 0.7$ Hz, 1H), 6.54 (dd, $J = 3.7, 1.8$ Hz, 1H), 2.80 (m, 2H), 1.75 (m, 2H), 0.99 (m, 3H); IR (cm^{-1}) (neat) 1675.

p-Methylbenzoylfuran (**3c**)

Oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, $J = 7.6$ Hz, 2H), 7.69 (dd, $J = 1.7, 0.7$ Hz, 1H), 7.28 (d, $J = 7.6$ Hz, 2H), 7.21 (dd, $J = 3.4, 0.7$ Hz, 1H), 6.59 (dd, $J = 3.4, 1.7$ Hz, 1H), 2.44 (s, 3H); IR (cm^{-1}) (neat) 1655.

2-Acetylthiophene (**3d**)

Oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, $J = 4.0, 1.0$ Hz, 1H), 7.64 (dd, $J = 5.0, 1.0$ Hz, 1H), 7.14 (dd, $J = 5.0, 4.0$ Hz, 1H), 2.57 (s, 3H); IR (cm^{-1}) (neat) 1662.

2-Propionylthiophene (**3e**)

Oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, $J = 3.8, 1.0$ Hz, 1H), 7.62 (dd, $J = 4.8, 1.0$ Hz, 1H), 7.12 (dd, $J = 4.8, 3.8$ Hz, 1H), 2.94 (m, 2H), 1.23 (t, $J = 7.2$ Hz, 3H); IR (cm^{-1}) (neat) 1668.

2-p-Methylbenzoylthiophene (**3f**)

Red solid: mp 70–72°C (lit.[14] 72°C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, $J = 8$ Hz, 2H), 7.69 (dd, $J = 4.2, 1.0$ Hz, 1H), 7.64 (dd, $J = 5.0, 1.0$ Hz, 1H), 7.29 (d, $J = 8$ Hz, 2H), 7.14 (dd, $J = 5.0, 4.2$ Hz, 1H), 2.44 (s, 3H); IR (cm^{-1}) (neat) 1634.

5-Chloro-2-acetylthiophene (**3g**)

Yellow solid: mp 45–46°C (lit. [15] 45.5–46°C); ^{1}H NMR ($CDCl_3$) δ 7.41 (d, $J = 4.6$ Hz, 1H), 7.01 (d, $J = 4.6$ Hz, 1H), 2.46 (s, 3H); IR (cm^{-1}) 1655.

5-Bromo-2-acetylthiophene (**3h**)

Yellow solid: mp 92–94°C (lit.[15] 94.5–95°C); ^{1}H NMR ($CDCl_3$) δ 7.43 (d, $J = 4.8$ Hz, 1H), 7.10 (d, $J = 4.8$ Hz, 1H), 2.50 (s, 3H); IR (cm^{-1}) 1650.

N-Methyl-2-acetylpyrrole (**5a**)

Oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (dd, $J = 4.0$, 1.6 Hz, 1H), 6.79 (t, $J = 2.4$ Hz, 1H), 6.11 (dd, $J = 4.0$, 2.4 Hz, 1H), 3.93 (s, 3H), 2.43 (s, 3H); IR (cm^{-1}) (neat) 1645.

N-Methyl-2-benzoylpyrrole (**5b**)

Oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.82 (m, 2H), 7.26–7.55 (m, 3H), 6.92 (dd, $J = 3.8$, 1.6 Hz, 1H), 6.74 (t, $J = 2.4$ Hz, 1H), 6.16 (dd, $J = 3.8$, 2.4 Hz, 1H), 4.03 (s, 3H); IR (cm^{-1}) (neat) 1650.

N-Methyl-2-(α-phenyl)acetylpyrrole (**5c**)

Oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.34 (m, 5H), 7.09 (dd, $J = 3.8$, 1.7 Hz, 1H), 6.82 (t, $J = 2.4$ Hz, 1H), 6.14 (dd, $J = 3.8$, 2.4 Hz, 1H), 4.07 (s, 2H), 3.91 (s, 3H); IR (cm^{-1}) (neat) 1646.

N-Methyl-2- octadecanoylpyrrole (**5d**)

Solid: mp 58–61°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (dd, $J = 4.0$, 2.0 Hz, 1H), 6.79 (t, $J = 2.0$ Hz, 1H), 6.12 (dd, $J = 4.0$, 2.0 Hz, 1H), 3.91 (s, 3H), 2.75 (t, $J = 7.6$ Hz, 2H), 1.66–1.70 (m, 2H), 0.88–1.31 (m, 31H); (ESI) MS 348.2 $(M + 1)^+$; IR (cm^{-1}) (neat) 1666.

3-Methyl-4-methoxylacetophenone (**7a**)

Oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.81 (m, 2H), 6.83 (d, $J = 8.4$ Hz, 1H), 3.88 (s, 3H), 2.55 (s, 3H), 2.24 (s, 3H); IR (cm^{-1}) (neat) 1649.

3-Methyl-4-methoxylbenzoylphenone (**7b**)

Solid: mp 75–78°C (lit.[16] 79.5–80.5°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.83 (m, 2H), 7.75–7.80 (m, 2H), 7.26–7.55 (m, 3H), 6.81 (d, $J = 8.4$ Hz, 1H), 3.88 (s, 3H), 2.32 (s, 3H); IR (cm^{-1}) (neat) 1643.

2-Methyl-4-methoxylacetophenone (**7c**)

Oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.72 (m, 1H), 6.69–6.74 (m, 2H), 3.80 (s, 3H), 2.54 (s, 3H), 2.50 (s, 3H); IR (cm^{-1}) (neat) 1647.

2-Methyl-4-methoxylbenzoylphenone (**7d**)

Solid: mp 72–74 °C (lit.[17] bp 219–221°C/23 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.78 (m, 2H), 7.51–7.53 (m, 1H), 7.39–7.44 (m, 2H), 7.32

(d, $J = 8.4$ Hz, 1H), 6.79–6.81 (m, 1H), 6.70–6.73 (m, 1H), 3.82 (s, 3H), 2.41 (s, 3H); IR (cm^{-1}) (neat) 1651.

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